

PATENT SPECIFICATION

DRAWINGS ATTACHED

1,047,920

Date of Application and filing Complete Specification: Oct. 21, 1965.

No. 44660/65.

Application made in Germany (No. Sch36014 IVb/12o) on Oct. 24, 1964.

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Index at acceptance:—C2 C2B20

Int. Cl.:—C 07 c 135/00

COMPLETE SPECIFICATION

Production of 3-Cyano-3,5,5-Trimethyl-1-Cyclohexanone

We, SCHOLVEN-CHEMIE AKTIENGESELLSCHAFT, a German Body Corporate, of Dorstener Strasse 227, Gelsenkirchen-Buer, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process and apparatus for the ————

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ERRATA

SPECIFICATION No. 1,047,920
Amendment No. 1

Page 2, line 1, before "by" insert "100%"
Page 2, line 44, for "over pressure" read
"overpressure"

THE PATENT OFFICE
8th December 1966

— is added thereto. The speed of reaction is regulated in such manner as to maintain constant reaction conditions and hydrocyanic acid concentration. Temperatures outside the range specified above produce insignificant or undesirable results. The reaction may be performed in the presence of a strongly polar solvent. 3-cyano-3,5,5-trimethyl-1-cyclohexanone is thus obtained with, for example, a yield of crude product of 70.5% of theoretical, from isophorone and hydrocyanic acid in dimethylacetamide and in the presence of 1.15% by weight of potassium carbonate at 160—175°C.

Finally it is known that a mixture of isophorone and hydrocyanic acid may be ducted over an alkaline catalyst placed on solid carrier substances, the hydrocyanic acid being employed in a quantity which does not exceed approximately 10% by weight of the total mixture brought into operation. This fully continuous, solid-bed process, which operates at 50 to 350°C, allows of yields of dihydro-isophorone-carbonic acid-nitrile exceeding 90%.

It has now been found that it is possible to produce 3-cyano-3,5,5-trimethyl-1-cyclohexanone with very high yields, i.e. over 95%, with short reaction periods and largely avoiding secondary reactions, by lowering the content of alkaline catalyst of the reaction mixture as compared to previous suggestions, i.e. the catalyst is employed



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We, SCHOLVEN-CHEMIE AKTIENGESSELLSCHAFT, a German Body Corporate, of Dorstener Strasse 227, Gelsenkirchen-Buer, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention relates to a process and apparatus for the production of 3-cyano-3,5,5-trimethyl-1-cyclohexanone. 5

It is known that 3-cyano-3,5,5-trimethyl-1-cyclohexanone may be produced by reacting isophorone and hydrocyanic acid in the presence of strongly alkaline catalysts to form cyanide ions.

10 It was suggested originally that a mixture of equimolar quantities of hydrocyanic acid, isophorone, sodium cyanide and sodium acetate in aqueous-methanolic solution be allowed to stand at room temperature for several days. After distillative processing, the 3-cyano-3,5,5-trimethyl-1-cyclohexanone was obtained in a yield of 75%, with an isophorone conversion of 65%. It is evident that a technique of this nature cannot be 15 considered for a technological process. Equally, suggestions to react isophorone and hydrocyanic acid in the presence of 0.1 mol of sodium cyanide per mol of isophorone in aqueous-methanolic solution at temperatures between 45°C and 60°C and reaction periods of 10 to 20 hours, by doing which yields of between 75 and 85% are obtained, are made for the laboratory scale only.

20 According to another known suggestion, the conversion of alicyclic olefinic ketones into the corresponding alicyclic cyano ketones is performed within a substantially higher temperature range, i.e. between 125 and 275°C, preferably between 150 and 225°C. The reaction occurs in the presence of strongly alkaline catalysts forming cyanide ions, which must be added in quantities of between 0.1 and 20% by weight 25 of the total weight of the reactants. This process is preferably performed intermittently, a part only of the ketone being initially charged to a heatable container together with the catalyst. A mixture of hydrocyanic acid and ketone is added thereto. The speed of its addition is regulated in such manner as to maintain constant reaction conditions and hydrocyanic acid concentration. Temperatures outside the range specified above 30 produce insignificant or undesirable results. The reaction may be performed in the presence of a strongly polar solvent. 3-cyano-3,5,5-trimethyl-1-cyclohexanone is thus obtained with, for example, a yield of crude product of 70.5% of theoretical, from isophorone and hydrocyanic acid in dimethylacetamide and in the presence of 1.15% by weight of potassium carbonate at 160—175°C.

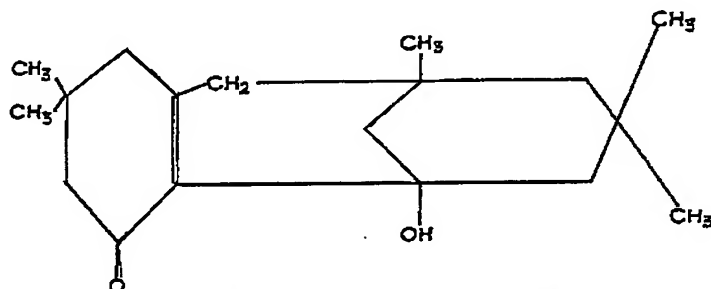
35 Finally it is known that a mixture of isophorone and hydrocyanic acid may be ducted over an alkaline catalyst placed on solid carrier substances, the hydrocyanic acid being employed in a quantity which does not exceed approximately 10% by weight of the total mixture brought into operation. This fully continuous, solid-bed process, which operates at 50 to 350°C, allows of yields of dihydro-isophorone-carbonic acid-nitrile exceeding 90%. 40

It has now been found that it is possible to produce 3-cyano-3,5,5-trimethyl-1-cyclohexanone with very high yields, i.e. over 95%, with short reaction periods and largely avoiding secondary reactions, by lowering the content of alkaline catalyst of the reaction mixture as compared to previous suggestions, i.e. the catalyst is employed

in quantities of less than approximately 10^{-1} to approximately 10^{-3} by weight of the reaction mixture.

Accordingly, the present invention provides a process for the production of 3-cyano-3,5,5-trimethyl-1-cyclohexanone comprising the step of reacting isophorone and hydrocyanic acid at a temperature between approximately 80 and 250°C in the presence of an alkaline catalyst present in an amount of approximately 10^{-1} to $10^{-3}\%$ by weight of the reaction mixture.

Apart from the fact that low alkaline concentration reduces the risk of hydrocyanic acid polymerisation, other secondary reactions are also prevented. Depending on temperature, isophorone forms different condensation or addition products in the presence of alkaline substances. Isophorone is converted, for example, at temperatures exceeding 80°C and at higher alkaline concentrations, into a hydroxy ketone of the formula:



This di-isophorone may however also be formed with yields of up to 30% at lower alkaline concentration, e.g. of 0.1% by weight in the conditions required for reaction with hydrocyanic acid. During batch reactions of isophorone and hydrocyanic acid it is appropriate therefore, to add a quantity of hydrocyanic acid equivalent to the alkaline substance after the addition of catalyst, even for the low alkaline contents in each charge suggested herein, before heating to the reaction temperature, in order to discourage the secondary reactions with isophorone even further. Such measures are superfluous in continuous operation.

The reaction may be performed in the presence of solvents. Another advantage of the present invention however resides in that homogeneity of the reaction mixture is assured at all times even in the absence of a solvent, at the low catalyst concentrations suggested, which is of particular importance for continuous performance of the process. At higher catalyst concentrations, a homogeneous mixture can be obtained only by addition of a solvent or mixture of solvents. If one omits the addition of a solvent, one obtains — in the cases last referred — active centres of high alkalinity on the surface of the undissolved cyanides, which in particular are responsible for the undesirable secondary reactions already mentioned above. One may if necessary employ a molar excess of isophorone, to act as a solvent.

For reasons of stability, the isophorone usual in the trade contains up to 10% of the isomeric beta-isophorone (3,5,5-trimethylcyclohex-3-ene-1-one). Equilibrium is established very quickly in the presence of alkaline substances at higher temperatures, so that the beta-isophorone portion is also converted into the 3-cyano-3,5,5-trimethylcyclohexanone by reaction with hydrocyanic acid. It was found that a conversion of the beta-isophorone is also accomplished with the quantities of catalyst suggested herein.

The temperatures required for the reaction lie between approximately 80 and 250°C, preferably between approximately 110 and 200°C. The process may be performed under normal pressure, raised or lowered pressure, with approximately identical yields. A negative pressure is frequently applied for hydrocyanic acid conversions. If an over pressure is desired, it is advisable to generate the same by means of an inert gas, for example, nitrogen.

All alkaline substances which form cyanide ions with hydrocyanic acid in the conditions of the reaction are fundamentally suitable as catalysts. Alkali metal cyanides, hydroxides and alcoholates are particularly suitable. By virtue of the homogeneity of the reaction mixture obtained with the present invention, the process is particularly appropriate for continuous operation. The accompanying drawing which is a flow diagram shows a plant in which a process according to the invention may be continuously performed.

Isophorone and hydrocyanic acid are pumped into a reactor RI from storage tanks A and B. A solution of 1% of ethyl sodium in isophorone is added by metering

at the same time from a storage tank C. The molar ratio between hydrocyanic acid and isophorone preferably does not exceed 1. The hydrocyanic acid is advantageously added at moderate speed. The HCN concentration of the reaction mixture in the reactor R I preferably does not exceed 5 g./litre. For operation under vacuum or under normal pressure, it is advantageous to equip the reactor R I with a reflux condenser, through which is fed in the isophorone which drips down in counterflow to the rising vapours and thus prevents entrainment of hydrocyanic acid. Corresponding to the quantities pumped in, reaction mixture is continually drawn off through the series-mounted subsidiary reactors R II and R III, whose gas spaces should not be in communication with that of the reactor R I, and conveyed to the scrubbing column W.

An acid aqueous solution, e.g. 0.5 to 1% HNO_3 solution flows therein in counterflow to the reaction product fed in at the foot, washing out the alkaline catalyst. To enhance the effectiveness of the scrubbing action, the scrubbing tower may be lined and/or be arranged as a pulsing column. The organic phase issuing from the head of the scrubbing tower is divided into three fractions in the distillation columns K I to K III, the fraction from column I, being an isophorone-water mixture, being returned to the scrubbing tower W, and the fraction from column II, being the excess of isophorone, being conveyed to the reactor R I through the storage tank A. Pure 3-cyano-3,5,5-trimethyl-1-cyclohexanone is obtained at the head of the column III.

The keto-nitrile obtained according to the invention may be employed for the production of diamines and amino-alcohols used for plastics.

In order that the invention may be more clearly understood some preferred embodiments thereof are now described, by way of example only.

EXAMPLES.

1. Intermittent operation.

50 litres of isophorone, 20 ml. of hydrocyanic acid and 280 ml. of a 15% methanolic NaOH solution, were placed in a 100 litres reactor equipped with stirring and venting devices. The reactor was heated to 150°C and 12.5 litres of hydrocyanic acid were fed in gradually over 4 hours. After a subsidiary reaction period of half an hour, the reaction product was pumped through a scrubbing tower filled with 0.65% nitric acid, from which it was ducted to a distillation column. Apart from 10.3 kg. of unconverted isophorone, the distillation provided 51.7 kg. of 3-cyano-3,5,5-trimethyl-1-cyclohexanone and 1.6 kg. of residue. This corresponded to a yield of 96.2%, related to converted isophorone, and of 97.9%, related to hydrocyanic acid employed.

2. Continuous operation.

8.5 litres of isophorone and 8.0 litres of a mixture of 21.5 litres isophorone and 10.5 litres of hydrocyanic acid were pumped per hour into the reactor R I in the accompanying drawing having a capacity of 100 litres and maintained at a temperature of 140°C , from the tanks A, B and C. One litre of a solution of 1.22 g. ethyl sodium in one litre of isophorone was simultaneously fed in per hour. This corresponded to a catalyst concentration of 0.007% by weight. After passage through the main reactor R I, with a mean dwell period of 4 hours, the reaction product passed through the two 30 litres secondary reactors R II and R III so as to have a secondary reaction period of 1 hour. The reaction mixture was thereafter passed into the sump of the scrubbing tower W in counterflow to a 0.65% nitric acid. The organic phase issuing from the head of the scrubbing tower was separated in the distillation column K I into a sump product and an isophorone-water mixture, the latter being returned to the scrubbing tower W, whereas the former was separated in the columns K II and K III into isophorone, 3-cyano-3,5,5-trimethyl-1-cyclohexanone and residue.

4.1 kg. of isophorone were obtained per hour at the head of the column K II. This corresponded to a conversion of 70.1%. The yield of 3-cyano-3,5,5-trimethyl-1-cyclohexanone drawn off at the head of column K III amounted to 10.9 kg. per hour, corresponding to a yield of 95.1% related to the isophorone, and 98.2% related to the hydrocyanic acid employed.

WHAT WE CLAIM IS:—

1. A process for the production of 3-cyano-3,5,5-trimethyl-1-cyclohexanone comprising the step of reacting isophorone and hydrocyanic acid at a temperature between approximately 80° and 250°C in the presence of an alkaline catalyst present in an amount of approximately 10^{-1} to $10^{-6}\%$ by weight of the reaction mixture.

2. A process according to Claim 1, wherein the reaction is performed in the absence of a solvent.

3. A process according to Claim 2, wherein the reaction is performed with a molar excess of isophorone.

4. A process according to any of the preceding Claims, wherein the reaction is a batch reaction additionally comprising the steps of adding an additional quantity of hydrocyanic acid equivalent to the alkaline catalyst.

5. A process for the production of 3-cyano-3,5,5-trimethyl-1-cyclohexanone substantially as hereinbefore described with reference to the accompanying drawing.

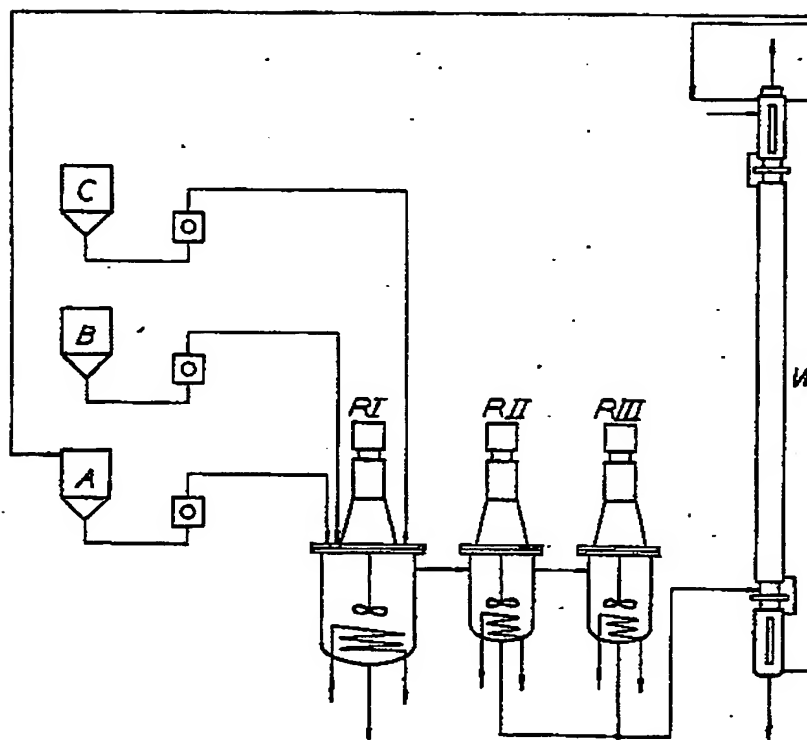
6. A process for the production of 3-cyano-3,5,5-trimethyl-1-cyclohexanone substantially as hereinbefore described in the foregoing Examples.

7. 3-cyano-3,5,5-trimethyl-1-cyclohexanone whenever produced by a process according to any of the preceding Claims.

8. An apparatus for carrying out a process according to any of Claims 1 to 7 constructed and arranged to operate substantially as hereinbefore described with reference to the accompanying drawing.

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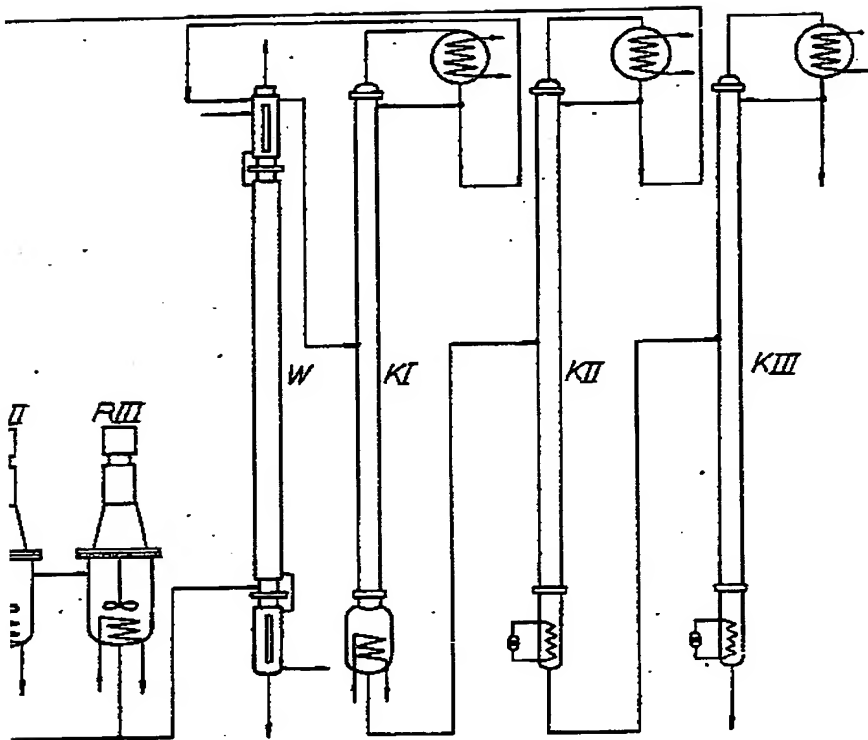


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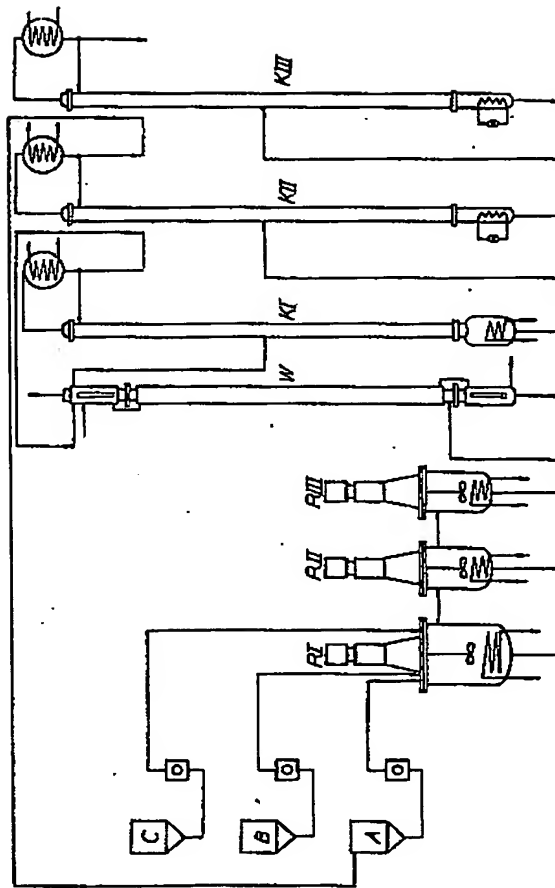
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